

Infrared Studies of Single Crystal C₆₀ : Silent and Higher Order Modes

Michael C. Martin

Department of Physics, BNL and SUNY @ Stony Brook

Carbon, one of the most abundant elements on earth, has been known for a very long time to exist in only two crystalline forms: graphite and diamond. However, within the past ten years a third form of carbon has been discovered: Fullerenes [1]. And after learning how to make and purify fullerenes in quantity [2], these novel cages of carbon have become quite heavily studied.

One of the most attractive features of fullerenes is their high symmetry. C₆₀, the most common fullerene, has the shape of a truncated icosahedron with *I_h* point group symmetry (Figure 1). This high symmetry can be exploited to predict the vibrational modes and electronic molecular orbitals of the molecule. While a 60 atom molecule will in general have up to 174 vibrational modes (3 x 60 - 3 translational - 3 rotational = 174), the *I_h* molecular symmetry causes many to be degenerate. The symmetries within *I_h* are

$$I_h = 2A_g \oplus 1A_u \oplus 3F_{1g} \oplus 4F_{1u} \oplus 4F_{2g} \oplus 5F_{2u} \\ \oplus 6G_g \oplus 6G_u \oplus 8H_g \oplus 7H_u ,$$

a total of 46 modes. The capital letters denote the degeneracy of the mode (*A* is singly degenerate, *B* is two-fold degenerate, *F* is 3-fold, *G* is 4-fold, and *H* is 5-fold) and the subscripts are *g* for *gerade* or even symmetry and *u* for *ungerade* or odd symmetry modes. Of these 46 only 10 are Raman-active (2 *A_g* and 8 *H_g*) and 4 are infrared-active (4 *F_{1u}*). These four *F_{1u}* modes were experimentally observed [2] at 527, 576, 1182, and 1438 cm⁻¹.

High-purity single crystals of C₆₀ were grown using a vapor transport method [3], and had sizes of approximately 1 x 1 x 0.5 mm. These crystals were then measured in the mid-IR (500-4000 cm⁻¹) at the U2B beamline and in the far-IR (50 - 600 cm⁻¹) using the U4IR beamline. Some crystals were placed inside a diamond anvil high pressure cell which was placed at the IR beam focus for measurements under pressure. These two beamlines' high IR brightness made good resolution measurements quick and easy to obtain. We present the infrared transmission data on a C₆₀ single crystal at 300 and 77K in Figure 2.

There are approximately 150 vibrational mode absorptions visible in the room temperature spectrum and many of the modes have a fine structure at low T. The four *F_{1u}* modes are seen to be so strong that they saturate with zero transmission in a range around the usual positions enumerated above. All the other

modes are approximately a factor of 100 times weaker than the 4 IR-active modes, and are now visible because of the significant thickness of the C₆₀ crystal. A similar set of weak vibrational modes was observed in Raman spectroscopy using a high laser power [5].

We looked for any sign of contaminants such as solvents, C₇₀ and C₆₀ O, but do not find evidence for any of these based on their known spectral features.

Many of the known Raman vibrational modes can readily be identified in our infrared spectra using their well known positions:

$H_g(2)$ at 431cm^{-1} , $H_g(3)$ at 709cm^{-1} , $H_g(4)$ at 775cm^{-1} , $H_g(5)$ at 1102cm^{-1} , $H_g(8)$ around 1576cm^{-1} , and $A_g(2)$ at 1470cm^{-1} . $H_g(7)$ at 1425cm^{-1} might also be active, but it is hidden under the extremely strong $F_{1u}(4)$ mode nearby. $H_g(1)$, $H_g(6)$, and $A_g(1)$ do not appear in our IR spectra.

The appearance of the Raman lines in the IR spectra strongly suggests that other IR-inactive resonances could appear in the spectra as well. However, the total number of lines far exceeds the number of vibrational modes, and the extension of the spectral features up to about 3200cm^{-1} indicates that combination modes are also present. Combination modes are weakly active in all molecular systems due to the anharmonicity of the bonds (they are not simple springs). This causes resonances at the sums and differences of two fundamental frequencies. Again group theory can be used to understand which combinations will be IR-active or Raman-active[3]; out of 2116 total possible combinations, 380 are IR-allowed and 484 are Raman-allowed. The binary combinations (involving two fundamentals) are expected to be stronger than third or higher order combinations. Indeed, the apparent absence of significant features above 3200cm^{-1} is in good agreement with the expected highest frequency of $\sim 1600\text{cm}^{-1}$ for the fundamental modes [4].

The energy of a particular combination mode $\nu_1 \nu_2$ is generally expected to be about $E(\nu_1) \pm E(\nu_2)$ (where $E(\nu)$ is the energy of mode ν). The Bose factors for fundamentals at ν_1 and ν_2 , n_1 and n_2 , respectively, appear in the intensity of the sum mode at $E(\nu_1) + E(\nu_2)$ as $1 + n_1 + n_2$, whereas for the difference mode $E(\nu_1) - E(\nu_2)$ the intensity is $|n_1 - n_2|$. Consequently, for the wavenumber range studied, the intensity of the difference modes should exhibit a strong decrease with temperature. None of the lines exhibit this behavior, therefore we must conclude that all of the resonances seen in our measurement are either fundamentals or should be close to the sum of two fundamental frequencies.

In many cases a broader high temperature line splits to several sharper low temperature resonances. This is illustrated in Figure 3, where spectra at several temperatures are plotted over an expanded scale for some particularly interesting frequency ranges. In the two middle panels of Figure 3 a few lines where the behavior is non-typical, in the sense that the oscillator strength seems to increase dramatically below the phase transition, are also pointed out. These lines were either very broad, or forbidden at high temperature. The significance of these resonances will be discussed later.

We used the group theoretical results of which combination modes are allowed together with the observed weakly active fundamental vibrations to come up with an assignment for all 46 vibrational modes [3]. This assignment enabled us to account for every observed vibrational mode in Figure 2, in the Raman higher-order data[5], and in agreement with neutron time-of-flight measurements [6]. The fact that we have observed Raman lines becoming weakly IR-active implies that there is a symmetry breaking occurring in the crystal; a given C₆₀ molecule no longer has its full I_h symmetry. Several possible

symmetry breaking mechanisms exist:

- Isotopic Impurities: ^{13}C is present in about 1.1% of natural carbon meaning that approximately 1/2 of all fullerenes will have one or more ^{13}C atoms, greatly reducing that molecule's symmetry.
- Solid State Effects: Each C_{60} molecule is at an FCC crystal site which imposes an additional FCC site symmetry on it. Other:
- Dislocations, foreign impurities, and surface effects can all change symmetries.

We can tackle the last item first. Since these are large single crystals the surfaces are a very small amount of the volume being probed and if they were the cause of spectral features, thin film measurements should have shown the same modes (they do not). Furthermore the intensity of all weakly-active features scales with the volume of the crystal. Random impurities and dislocations can be ruled out because of the detailed confirmation of our spectra shown in [Figure 2](#) obtained on samples grown by several groups around the world [\[7\]](#), [\[8\]](#)

Isotopic activation of previously silent modes is possible to test. We obtained a sample that was grown from 8% enriched ^{13}C fullerenes and repeated the measurements [\[9\]](#). The spectra obtained were quite similar to the ones obtained in [Figure 2](#). The relative intensities of each feature did not significantly change, and each mode was broadened somewhat. These effects could be well modeled by simply assuming the known mass distribution and applying this broadening function point-by-point to the natural abundance C_{60} spectrum. Furthermore a theoretical model of C_{60} was used to calculate the IR spectrum with 1.1% and 8% probability of any atom being a ^{13}C [\[9\]](#). The resultant calculated spectrum is displayed in [Figure 4](#) and shows firstly that the modes activated by this mechanism are approximately 10^4 times weaker than the allowed F_{1u} modes whereas our measurements find modes only 10^2 times weaker implying that the true symmetry breaking is significantly stronger than that due to the addition of a proton. Secondly, the calculation shows that indeed the intensity of each weakly active mode should be enhanced by an average factor of 4.45, which we do not observe. We can therefore conclude that while ^{13}C may cause a symmetry-lowering, this is a much weaker effect than we are observing.

Finally that leaves us with the effects of the fullerene molecules being located in a crystalline solid. The FCC site symmetry that is imposed on a C_{60} will reduce the symmetry, however in all cases it will retain the inversion symmetry. This means that *gerade* and *ungerade* modes will retain their even and odd characters, and therefore Raman modes will not be active in the infrared as well as the reverse. Since we clearly do observe Raman modes in [Figure 2](#), this again seems to not be our symmetry-breaking mechanism. Furthermore, in the high temperature state (greater than 250K) the fullerenes are freely rotating which would "smear out" any solid state effects. If on the other hand the vibrational states were sensitive to the neighboring molecules on a much faster time scale than the rate of rotation, each molecule would see a "snapshot" of its neighbors having essentially random orientations. In this case the site symmetry will be much lower than FCC and the inversion symmetry would no longer hold.

To explore if these "snapshot" ideas are viable, we developed a model system where we could calculate what the relevant time scales are [\[10\]](#). We found that activation of symmetry-forbidden modes indeed does occur as long as the lifetime of the vibrational mode, as deduced from its width, is shorter than the rate of motion of the molecules. We have termed this effect "motional diminishing", in analogy with

motional narrowing in NMR, since the result of increasing the motion will remove symmetry lowerings and forbidden vibrational modes will again be disallowed (they will diminish).

To apply these ideas to the present case, we need to know the natural lifetime of a particular vibrational mode, and the correlation time of the fluctuations of the neighboring fullerenes. The lifetimes of the weakly active fundamentals can be inferred from measured line widths, approximately $3 - 6\text{cm}^{-1}$, corresponding to lifetimes of $5 - 10\text{psec}$. The correlation time is related to the rotational diffusion constant which was measured by neutron scattering measurements to be $D_R = 1.4 \times 10^{10}\text{sec}^{-1}$ at $T=260\text{K}$ [11], just above the rotational phase transition. Since we have observed forbidden modes at this temperature, the correlation time must be greater than 10psec , which corresponds to a rotation by a C_{60} by an angle of greater than 5 degrees.

As the temperature is raised, the rate of rotation of the fullerenes will increase. However the lifetime of the vibrational modes will also decrease since in insulators the primary channel of phonon decay is due to the interaction between phonons and the enhanced population of phonons at higher temperatures will lead to shorter lifetimes. Therefore as the temperature is further increased the "forbidden" lines should either

1. motionally diminish (if the lifetime of the resonance has a weaker temperature dependence than the rotational motion), or
2. the integrated intensities will not change while the line widths increase (the mode lifetime remains shorter than the fluctuation time at all temperatures).

To test these predictions we measured the IR spectrum of a C_{60} crystal at elevated temperatures. All observed modes do broaden without a significant change in integrated intensities up to a temperature of 650K .

Motional diminishing can, however, be observed in a few narrow lines which are only active in the low temperature (less than 250K) state. Figure 3 demonstrates such modes at $1566, 1314\text{cm}^{-1}$ (middle panels with arrows) and four very sharp modes in the $750 - 765\text{cm}^{-1}$ region. These modes are active in the low temperature state where rotation is inhibited, then completely disappear just above the rotational transition temperature. The linewidths of these modes, $0.7 - 1.5\text{cm}^{-1}$, are narrower (and therefore they have longer lifetimes) than the other weakly active fundamentals which persist to higher temperatures. We can now establish an experimental limit on the correlation time τ between neighboring C_{60} molecules in the rotating state: τ between 10psec and 20psec . Combining these times with the measured rate of rotation [11] we find they correspond to rotation angles of between 5 and 10 degrees.

The merohedral disorder observed in the low temperature phase suggests that fullerene [12] molecules are sensitive to whether a neighboring ball has a bond or a pentagon or hexagon center facing it. The amount of rotation needed to move between these two arrangements is approximately 15 degrees so it is reasonable that a 10 degree rotation will significantly change the crystal field perturbations being applied to a fullerene molecule.

To conclude, we have shown how experiments at the NSLS have led to the discovery of weak symmetry breaking in the IR spectra of C_{60} single crystals. In addition, this molecule is found to be a complex system where second and higher order combination modes can be studied. In trying to elucidate the mechanism of the weak symmetry breaking we first ruled out the most obvious symmetry lowering due

to ^{13}C atoms within individual C_{60} molecules. The effective crystalline environment was found to be much more disordered than initially thought, making fullerite above the rotational transition temperature a plastic crystal system. The lifetime of nearly all fundamental vibrational modes turns out to be shorter than the rotational diffusion time constant and therefore the molecules "see" a static, disordered configuration of neighbors giving rise to the symmetry breaking which is observed. A few fundamental modes are found to exhibit the newly understood motional diminishing phenomena.

This work was done in collaboration with Laszlo Mihaly, Xiaoqun Du, John Kwon, Jaroslav Fabian (SUNY @ Stony Brook), J. Goddard (Orsay, France), P. Bernier and J.M. Lambert (Montpellier, France). Support was primarily by NSF grant DMR9202528, and also by NSF grant DMR9118414 (J.F.) and from CNRS through the Groupe de Recherche 1019 (J.G, P.B, J.M.L.). The NSLS is supported by the U.S. Department of Energy, under contract DE-AC02-76CH00016. [1] H.W. Kroto, J.R. Leath, S.C. O'Brien, R.F. Curl, and R.E. Smalley, Nature 318, 162, (1985).

[2] W. Kratschmer, L.D. Lamb, K. Fostiropoulos, and D.R. Huffman, *Nature***347**, 254, (1990).

[3] Michael C. Martin, Xiaoqun Du, John Kwon, and Laszlo Mihaly, *Phys. Rev. B***50**, 173, (1994).

[4] For a review, see A.F. Hebard, *Physics Today*, November 1992, p.26.

[5] Z.-H. Dong, P. Zhou, J.M. Holden, P.C. Eklund, M.S. Dresselhaus, and G. Dresselhaus, *Phys. Rev. B***48**, 2862, (1993).

[6] C. Coulombeau, H. Jobic, P. Bernier, C. Fabre, D. Schultz, and A. Rassat, *J. Phys. Chem.***96**, 22, (1992).

[7] R. Winkler, T. Pichler, and H. Kuzmany, *Z. Physik B***96**, 39, (1994).

[8] K. Kamaras, K. Matsumoto, M. Wojnowski, E. Schšnherr, H. Klos and B. Gotschy, in "Progress in Fullerene Research", Eds. H. Kuzmany, J. Fink, M. Mehring and S. Roth, *World Scientific*, p. 357, (1994).

[9] Michael C. Martin, J. Fabian, J. Godard, P. Bernier, J.M. Lambert, and L. Mihaly, *Phys. Rev.***51**, 2844, (1995).

[10] Michael C. Martin, and Laszlo Mihaly, *to be published*.

[11] R. Tycko *et al.*, *Phys. Rev. Lett***67**, 1886, (1991); D.A. Neuman *et al.*, *Phys. Rev. Lett.*, **67**, 3808, (1991).

[12] P.A. Heiney, J.E. Fisher, A.R. McFhie, W.J. Romanow, A.M. Denesteyn, J.P. McCauley Jr., A.B. Smith III, and D. Cox, *Phys. Rev. Lett.***66**, 2911, (1991).

This document is maintained by the [NSLS User Administration Office](#).

[DISCLAIMERS](#) : Revised Date : July 24, 1996
